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ScienceDirect
Procedia Engineering 130 (2015) 1788 – 1794
Procedia Engineering
www.elsevier.com/locate/procedia

14th International Conference on Pressure Vessel Technology

In-Situ Strain Gauge: Based on Photoluminescence of Quantum Dots

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Abstract

Due to that the spectra of CdSe/ZnS core/shell nanocrystals showed a wavelength shift when under external pressures, researches are conducted to design a wavelength shift-based strain or stress gauge. However, the spectrum's shift can only be subtly sensitive when the pressure applied to nanocrystals reaches GPa， which makes the gauge hard to be applied to practice. In this paper, it was found that the photoluminescence(PL) intensity of CdSe/ZnS core/shell quantum dots (QDs)epoxy resin composites changes significantly with strain. Meanwhile, the changes remains stable after 3-5 cycles. We coated the QDs-epoxy resin composites on the surface of metal tensile sample, the PL intensity and strain changes synchronously. In addition, it has been successfully proved that the variation of QDs' concentrations along with the strain is the main reason for the photoluminescence intensity changing. This research has shown the possibility that this kind of nanocomposite can be designed as a new strain gauge to quantitatively detect stress or strain in-situ by being coated on the structure surface.

Peer-review under responsibility of the organizing committee of ICPVT-14

Keywords: Strain gauge; quantum dots; photoluminescence; nanocomposite; paintcoat.

1. Introduction

Stress and strain are two important parameters for measuring the health of structure. There are already many methods to detect stress and strain in engineering [1]. Among them, thanks to advantages of high resolution, small

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Peer-review under responsibility of the organizing committee of ICPVT-14
doi:10.1016/j.proeng.2015.12.335

error and relatively low price, bonded electrical resistance strain gauge is widely applied [2].However, these traditional strain gauges can't meet the requirements of large area or non-contact stress or strain detection [3,4]. Recently, reports have shown that, utilizing the variation of QDs' fluorescence intensity in response to the tension and the pressure, the QDs epoxy resin composites coating may conquer the barrier.

Quantum dots, as fluorescence nano-semiconductor materials, are currently being used in fields of biological probes [5] and electronic displays [6,7]. Apart from dots, fluorescence nanocrystals also include nanorods and tetrapods. Experiments have shown that emission wavelength of CdSe/CdS core/shell quantum dots, nanorods, and tetrapods all have blue or red shift in response to external pressure. Because of different geometry among dot, rods and tetrapods, they have different spectral change features [8]. Attempts were conducted to measure strain or stress by using the spectral change of QDs' fluorescence [9,10]. Furthermore, researchers have used tetrapod nanocrystals to make stress gauge [11,12]. However, for quantum dots, because of their small sizes (3-5 nm) and isotropic shapes, their wavelength shift only when external pressures reach GPa [8].

To solve this problem, researches were conducted to study how QDs' PL intensities change when QDs are under pressure [13].Experiments demonstrated that PL intensity enhance along with the increase of compressive stresses. This paper respectively investigated QDs PL intensity change in response to tension strains and pressure strains. Results shows that PL intensity decreases with the increasing of the tension strain, while increases with the increasing of compressive strain. Afterwards, this kind of nanocomposite were coated on the surface of metal tensile specimen for 5 loading and unloading cycles. The experiment result showed that the PL intensity and strain almost keep changing synchronously. Experiments also showed that the change of the concentration of QDs with strain is the main factor of PL intensity changing. All these were telling the possibility that QDs can serve as a strain gauge by coated on the surface of structures, which is capable of measuring forces or deformations in-situ.

2. Experimental

CdSe/ZnS core/shell QDs were synthesized by the micro reactor technology[14-16], with an average size of 2-3nm(blue) or 4-5nm(green), characteristic absorption peaks at 469nm or 528nm, respectively. Because of the low viscosity and the fluorescence wavelength different from QDs, a bisphenol-A type epoxy resin and modified amine curing agent were selected as carrier of QDs. Dissolve the QDs powder with chloroform, then use ultrasound to make the QDs completely dispersed. Add the solution to the epoxy resin and stir the mix resin at 50 ℃ for 1 h to make chloroform evaporate as much as possible. After curing agent being mixed with resin, pour the mixed solution into the mold. The filled molds were then put into an oven at 80℃ for 6 h. After the molds cooling down, the tensile specimen (dumbbell shaped) and the cuboid compression specimen (10×10×30 mm) were obtained.

In order to investigate the relationship between fluorescence intensity and strain of QDs-epoxy resin nanocomposite, tensile and compressive tests were performed with the tensile and compressive samples, and the change of the fluorescence intensity was recorded at the same time. Excitation light was provided by 365 nm UV LED light and the spectra data were obtained by spectrometer(Ocean Optics, QE65-Pro-FL). The distance from the spectrometer probe to the sample surface was constant. In tensile and compressive tests, tensile specimens were stretched with a constant loading rate of 60N/min until fractured, and compression specimens were compressed with a constant rate of 0.12mm/min until the cuboid compression specimens appeared obvious bulging or bending. Also the tensile specimens were used to carry out the load and unloading cycles test for 3 times, and the cyclic variations of the fluorescence intensity were recorded synchronously. The load first charges from 10 N to 200 N, then discharges to 10N. Loading and unloading rates kept at 60 N/min.

Also, the nanocomposites of QDs epoxy resin were coated on the surface of metal tensile specimen by the spin-coating method. A thin film layer with uniform thickness on the sample surface was obtained after drying in the oven at the 80 ℃ for 6 h. Then the cycle uniaxial tensile tests were performed on the universal testing machine (MTS-SANS, CMT5504) with the metal tensile specimen coated with QDs-epoxy resin nanocomposite. The samples were loaded or unloaded with the rate of 0.5 kN per 5 seconds and then hold load for 5 seconds until it reaches the max load 5.5 kN or min load 0.5 kN. In order to ensure the metal samples were in elastic range, the maximum load was constrained to 5.5 kN. The spectrum was recorded every 0.5 kN.

In order to study the QDs' sizes' influences to the relationship between fluorescence intensity and QDs-epoxy resin composites' strain, an experiment was conducted by adding two different sizes QDs (2-3 nm, 4-5 nm) into tensile specimen. The concentrations of the two QDs need to be kept the same, to exclude the possible effect of to the results.

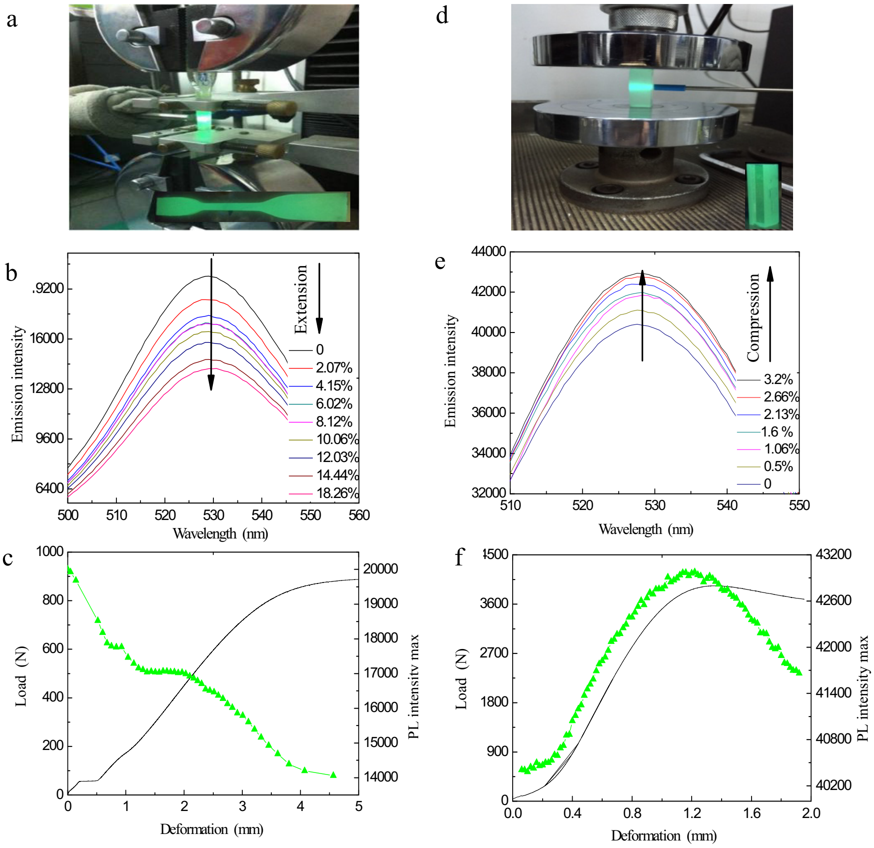

Fig. 1. Tensile and compressive tests of the QDs-epoxy resin nanocomposite. (a) Tensile specimen and tensile device. (b)Spectra from 9 different deformation of tensile specimen. (c)The max PL intensity variation with the tensile deformation increasing. (d)Compressive specimen and compressive device. (e) Spectra from 7 different deformation of compressive

Finally, the tensile samples with different deformation were observed by high-resolution transmission electron microscope(HRTEM) to investigate the concentration changing of QDs in the nanocomposite. The forces of 0 N, 900 N, 1100 N and 1300 N were respectively loaded on the four same tensile specimens, and the tensile strains of four specimens were 0,14.4%, 22.4%, 28.4%, respectively. Then slices were cut from the stretched tensile specimens along the strain direction by slicing machine (Leica EM UC7)with the thickness of 60 nm. Concentration of QDs in the slices can be observed through HRTEM images.

3. Results and discussion

The experimental apparatus and results of tensile and compressive tests of the QDs-epoxy resin nanocomposite are shown in Fig. 1. Along with the increase of extension rate, QDs PL intensity presents a clear decrease(Fig. 1b),the PL intensity decrease by 29.75% when the elongation of the sample increase from 0 to 18.26%. Fig. 1c shows that the peaks of PL intensity decrease with the increase of the deformation during the whole stretching process. However, the change of PL intensity during compression process is the opposite of the tensile process. As shown in Fig. 1e, the PL intensity increase with the increase of the compression ratio, and the PL intensity increase by 5.80% when compression ratio increase from 0 to 3.73%. Fig. 1f showed that the changes of the PL intensity peak with the compressive deformation during the whole compression process, before the compression reached the yield, the PL intensity peak increase with the increase of compression ratio, and the opposite trend appeare after the yield. The reason why the opposite trend occurred is that the specimen bent after compressed to the yield, which make the sample surface stay away from the fiber probe.

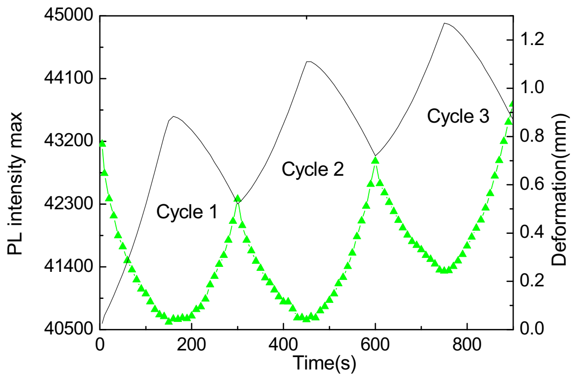

Fig. 2. The max PL intensity variation with the tensile deformation during 3 loading and unloading cycles.

Figure 2 demonstrated the relationship between the PL intensity peak and tensile deformation during three loading and unloading cycles. Duration, the PL intensity peak and deformation kept a reciprocal ratio. Because of residual strains, deformations accumulated.

The clear resemblance between the curve of PL intensity-Times and the curve of Deformation-Times is shown in Fig. 3.The two curves reached the peak or the minimum in the same moment, which demonstrates the changing between PL intensity max and deformation have the desirable time synchronization. The change law keep stable during the 5 cycles, which indicates that this nanocomposite can be used for detecting strain circularly.

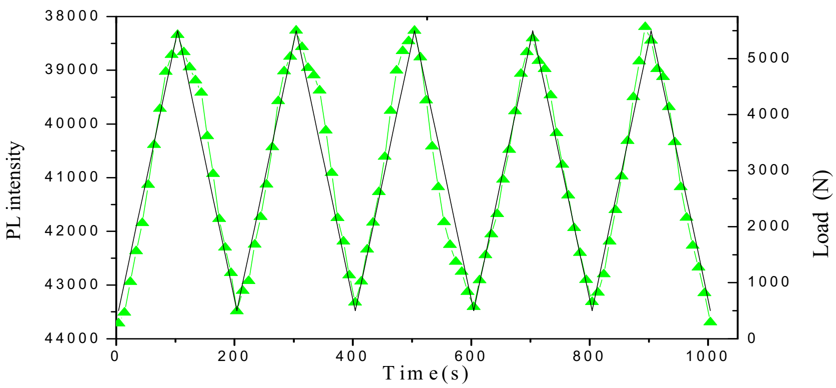

Fig. 3. The max PL intensity of the QDs-epoxy resin nanocomposite thin film variation with the deformation of metal tensile specimen.

Figure 4 shows that when adding two different sizes of quantum dots, the emission peaks of different wavelengths keep the same changing trend with the tensile deformation of the specimen. As shown in Fig. 4a, 469nm is the wavelength of the QDs with the size of 2-3 nm,and 528 nm is the wavelength of the QDs with the size of 4-5nm. The change of spectral curves at the wavelength spots are similar. Fig. 4b shows during the whole tensile process, PL intensity peaks of two different size QDs change along with the deformation in a almost same trend. When the elongation of the sample increased from 0 to 30%, the peak intensity of blue QDs decreased by 14.3%, and green QDs decreased by 15.1%.

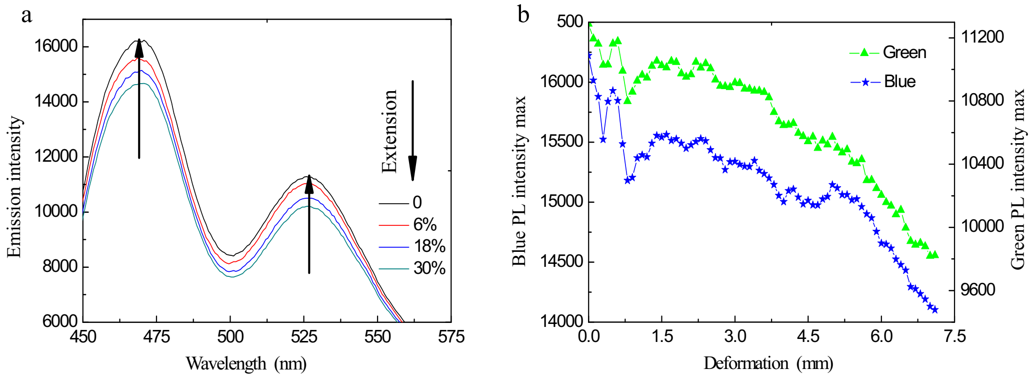

Fig. 4. The relationship between PL intensity and deformation of two different size QDs. (a)The Spectra of two size QDs both down shift with increasing of tensile deformation. (b)The PL intensity of two size QDs both decrease with increasing of tensile.

Figure 5 shows that the concentration of the QDs in samples decreases significantly with the increasing of deformation. From the HRTEM images for four different deformation(0,14.4%,22.4%,28.4%)samples, the number of QDs in the same area(a visual field) reduces gradually.

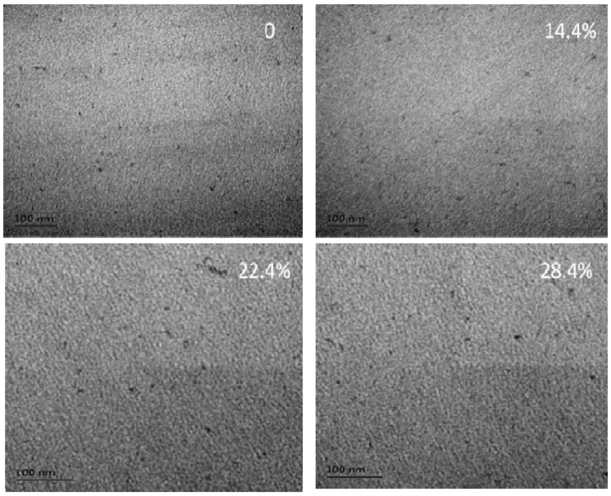

Fig. 5. HRTEM images of QDs-epoxy resin nanocomposite with different deformation.

All experimental results showed that, when QDs-epoxy resin nanocomposites were stretched or compressed, the PL intensity would change significantly along with the deformation. And this relationship maintained during the whole three cycles, which make this QDs-epoxy resin nanocomposite possible to be designed as a new in-situ strain gauge. In these tensile or compressive tests, the stress of the specimens are less than 50MPa. But researches and experiments conducted by other research groups or institutions have revealed that PL intensity of QDs do not change, even when they are under 100MPa [13]. So the load will not directly affect the PL intensity of a single quantum dot.

Meanwhile, Fig. 4 showed that the responses of different sizes QDs' PL intensities to the strains stay almost constant, which proved that the size of the QDs do not affect the relationship between the PL intensity and strain. The observation results of HRTEM show that, after being stretched in different degrees, the concentrations of QDs in the nanocomposites changed. The higher elongation was, the lower concentrations were. So here we can conclude, that the concentrations of QDs changed with the material strains, which led to the amount of QDs decrease or increase within the probe area, and fluorescence intensity of nanocomposite then changed. However, the refractive index and transmissivity of epoxy resin may change with deformation, which may have certain effect to PL intensity. This factor was not considered in our experiment.

4. Conclusion

We have designed a kind of QDs-epoxy resin material whose PL intensity is sensitive to strain. After a series of experiments, we have successfully proved that, due to the strain, the change of QDs' concentration would lead to the change of PL intensity. Thanks to this characteristic, the QDs epoxy resin composites can be utilized into a new in-situ strain gauge. Traditionally, most strain gauges make use of wavelength shifts caused by QDs' being loaded with GPa force. Different from those gauges, the detection range of our nanocomposite strain gauge can reach the level of MPa or less. And this kind of nanocomposite material is easy to produce. Just being coated on the structural surface, our nanocomposite gauge is able to monitor the stress or strain by noncontact detection. But in this experiment, we only take the influence of concentration into consideration. Other factors, such as material refractive index, transmittance and the phenomenon of agglomeration of quantum dots, will be investigated in future experiments.

Acknowledgements

This investigation was supported by the National Natural Science Fund of China (51172072, 51475166) and the National Basic Research Program of China (2013CB035505).

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